

An *In Situ* X-Ray Absorption Spectroscopy Study of InSb Electrodes in Lithium Batteries

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Recently we have reported on several intermetallic compounds such as η' -Cu₆Sn₅ and InSb that exhibit promising electrochemical properties as negative insertion electrodes for lithium batteries.¹⁻³ We have performed detailed studies of the electrochemical reaction of lithium with InSb using *in situ* EXAFS. In these materials the reaction progresses by a mechanism of lithium insertion/metal displacement from a Sn or Sb array of atoms.²⁻⁴

Previous electrochemical studies indicated that the zinc-blende structure of InSb is "conditioned" during the initial electrochemical reaction with lithium;^{2,3} thereafter, the InSb electrode cycles reversibly over several distinct plateaus between 1.2 and 0.5 V. During lithium insertion, the fcc Sb array in InSb ($a = 6.478 \text{ \AA}$) remains intact and yields Li₃Sb ($a = 6.572 \text{ \AA}$).⁵⁻⁶ On extrusion of metallic In, only a 4.4% volume expansion results, neglecting the volume of the extruded In. Data from *in situ* x-ray diffraction and cyclic voltammetry strongly suggest that the stability of the fcc Sb array plays an important role in the reversibility of the electrochemical reaction.

Figure 1 shows the distribution of In-containing phases over a charge cycle. At the start of the charge, the distribution of the indium in the electrode was approximately 70% as LiIn (lithiated In metal), 20% as In metal, and up to 10% as Li_xIn_ySb. Upon charging, LiIn first reverts to metallic In on a voltage plateau at 0.62 V. The In metal content at the end of the first plateau is approximately 90%. Near the top of the charge the amplitude of the nearest-neighbor In-Sb path is smaller than in the initial electrode material, indicating that the displaced In has not been entirely reincorporated into the Li_xIn_ySb phase. In fact, quantitative evaluation shows that as much as 40% of the indium remains as In metal, outside the Sb framework.

In the subsequent cycle, the cell was discharged from 1.2 V to 0 V. In a reversal of the processes that have been described for the charge, In is extruded from the Sb (fcc) array and replaced by Li. At about 0.5 V, where 80% of the In is present as a metal, Li begins to react with the In metal, forming LiIn.

The Sb-edge EXAFS data confirm that the Sb array remains intact throughout and incorporates Li to form a compound approaching Li₃Sb; a small quantity of In remains in the lattice. However, at the top of the charge, after 60% of the In has been reincorporated into the Sb lattice, Li continues to be removed without a commensurate increase in the In content. As a result, at the top of charge the electrode has a defective zinc-blende structure with up to 40% vacancies on the In site.

After one "conditioning" cycle, the cell cycles well when limited to the range where the primary mechanisms are Li insertion and In extrusion (above 0.5 V), even though a significant fraction of the In is not reincorporated into the Sb framework. This explains the loss of capacity observed between the conditioning cycle

and the following cycles. The cell exhibits a reduced reversible capacity when discharged below 0.5 V, when Li reacts with the extruded In to form LiIn.

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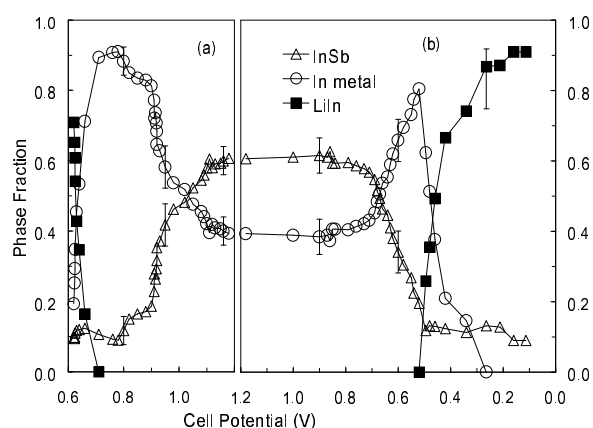


Figure 1. Distribution of In-containing phases, Li_xIn_ySb (triangles), metallic In (circles), and LiIn (squares) as a function of cell potential upon charging (panel a) and discharging (panel b). Error bars are shown for representative points.⁴